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Silicone and highly fluorinated elastomers show by far the greatest resistance to high temperatures ( $\geq 200\text{ }^{\circ}\text{C}$ ). Figure 7.1 illustrates the difference in chemical degradation at  $203\text{ }^{\circ}\text{C}$  between typical NBR and FKM compounds. However, at less elevated temperatures, other factors (e.g., mechanical strength) may cause other elastomers to be preferred. Under thermal aging, all chlorine-containing elastomers (e.g., epichlorhydrin) may evolve hydrogen chloride gas if insufficient acid acceptor is present or if temperatures are high enough. Fluorine-containing elastomers may evolve hydrogen fluoride gas, and so, in extreme circumstances, appropriate care should be exercised.

Thermal degradation is an extreme case of the chemical relaxation mechanisms outlined in Section 7.2.4.

## 7.6 Effect of Fluid Environments

The flexibility associated with an elastomer – essential for performing its many functions (sealing, isolating vibrations, etc) – stems from the 10% or so of space between its molecules – the “free volume.” However, this internal space leads to other, less welcome characteristics: it provides the physical means for fluid molecules to enter the elastomer. No elastomer is completely resistant to chemical and/or physical effects arising from contact with fluids. Different elastomers can withstand such attacks to different extents. If a rubber absorbs a large volume of liquid, it generally becomes weak and useless for most engineering applications. Moreover, chemical attack can cause further deterioration. In either case, initial weakening is progressive; in the latter case, weakening or embrittlement continues throughout service life. It is clear from these observations that the durability of an elastomeric component is affected by its environment. Elastomer selection therefore needs to include a considerations of the service fluid composition. Organic liquids tend to weaken elastomers by physical means only, whereas corrosive liquids, such as acids and alkalis, tend to attack chemically.

Rubber and ebonite are used as coatings and linings to protect chemical plant, pipes, and other equipment against corrosion and abrasion. In that context, they may come into contact with various chemical solutions. Table 7.3 summarizes the resistance at room temperature of several elastomer types to a range of aqueous and other liquids; the behavior may, however, be different at elevated temperatures. Such tables are inevitably very approximate and should be used for preliminary guidance only, since different results may be obtained with different compounds of the same base elastomer. Also, different applications may render the same elastomer compound satisfactory or unacceptable, even with the same liquid. Many such tables are provided by materials producers and manufacturers, and before concluding that the classification is relevant for the application at hand, the engineer should always inquire exactly which tests were performed to determine the classification and whether the formulation of the elastomer compound is suitable.

Oil and gas can come into direct contact with rubber in downhole applications in the exploration for and production of hydrocarbons. The rubber may be exposed in the form of seals, flex joints or flexible pipes, hoses, etc., to crude oil containing methane and other hydrocarbon gases, hydrogen sulfide, and/or carbon dioxide gases, often at elevated

**Table 7.3** Chemical Resistance of Several Types of Rubber and Ebonite: S, Satisfactory; L, Limited Applications; X, Not Recommended

| Chemical environment                | NR and SBR |         | NBR  |         | Butyl | Poly-chloro-prene | Chloro-sulfonated polyethylene |
|-------------------------------------|------------|---------|------|---------|-------|-------------------|--------------------------------|
|                                     | Soft       | Ebonite | Soft | Ebonite |       |                   |                                |
| <i>Acids</i>                        |            |         |      |         |       |                   |                                |
| Acetic (glacial)                    | X          | S       | L    | S       | L     | X                 | S                              |
| Aqua regia                          | X          | X       | X    | X       | X     | X                 | X                              |
| Chlorine water                      | L          | S       | L    | S       | X     | X                 | S                              |
| Chromic, 50%                        | X          | X       | X    | X       | X     | X                 | L                              |
| Hydrochloric                        | S          | S       | L    | S       | S     | L                 | S                              |
| Hydrofluoric, 50%                   | S          | S       | L    | L       | S     | L                 | S                              |
| Nitric, 20%                         | X          | X       | X    | X       | S     | X                 | S                              |
| Nitric,40%                          | X          | X       | X    | X       | X     | X                 | S                              |
| Nitric, fuming                      | X          | X       | X    | X       | X     | X                 | X                              |
| Phosphoric, 80%                     | L          | S       | L    | S       | S     | L                 | S                              |
| Sulfuric, 25%                       | S          | S       | L    | S       | S     | S                 | S                              |
| Sulfuric, 50%                       | S          | S       | L    | S       | S     | L                 | S                              |
| <i>Inorganic Salts and Alkalies</i> |            |         |      |         |       |                   |                                |
| Alums                               | S          | S       | S    | S       | S     | S                 | S                              |
| Ammonia, 25%                        | S          | S       | S    | S       | S     | S                 | S                              |
| Ammonium hydroxide                  | S          | S       | S    | S       | S     | L                 | S                              |
| Copper Chloride                     | L          | S       | S    | S       | S     | S                 | S                              |
| Ferric Chloride                     | L          | S       | S    | S       | S     | L                 | S                              |
| Ferrous sulfate                     | S          | S       | S    | S       | S     | S                 | S                              |
| Potassium hydroxide                 | S          | S       | L    | S       | S     | S                 | S                              |
| Silver nitrate                      | L          | S       | L    | S       | S     | S                 |                                |
| Sodium thiosulfate                  | S          | S       | S    | S       | S     | S                 | S                              |
| Zinc chloride                       | S          | S       | S    | S       | S     | S                 | S                              |
| <i>Organic Materials</i>            |            |         |      |         |       |                   |                                |
| Acetone                             | S          | S       | X    | S       | S     | X                 | S                              |
| Alcohols                            | S          | S       | S    | S       | S     | L                 | S                              |
| Cresol                              | X          | X       | X    | X       | X     | L                 | X                              |
| Ethers                              | X          | X       | S    | X       | L     | L                 | S                              |
| Ethyl glycol                        | S          | S       | S    | S       | S     | S                 | S                              |
| Fatty acids                         | X          | L       | L    | L       | L     | L                 | L                              |
| Glues                               | S          | S       | S    | S       | S     | S                 | S                              |
| Glycerine                           | S          | S       | S    | S       | S     | S                 | S                              |
| Hexane                              | X          | X       | S    | S       | X     | S                 | S                              |
| Methyl chloride                     | X          | X       | X    | X       | L     | X                 | X                              |
| Mineral oils                        | X          | L       | S    | S       | X     | L                 | S                              |
| Petroleum oils                      | X          | L       | S    | S       | X     | L                 | L                              |
| Phenol                              | L          | S       | X    | S       | L     | X                 | X                              |
| Soap solutions                      | S          | S       | S    | S       | S     | S                 | S                              |
| Turpentine                          | X          | X       | S    | S       | X     | X                 | X                              |
| Vegetable oils                      | X          | L       | S    | S       | S     | L                 |                                |

Table 7.3 *cont*

| Chemical environment     | NR and SBR |         | NBR  |         | Butyl | Poly-chloro-prene | Chloro-sulfonated polyethylene |
|--------------------------|------------|---------|------|---------|-------|-------------------|--------------------------------|
|                          | Soft       | Ebonite | Soft | Ebonite |       |                   |                                |
| <i>Plating Solutions</i> |            |         |      |         |       |                   |                                |
| Brass, copper, lead      | S          | S       | S    | S       | S     | S                 | S                              |
| Chromium                 | X          | X       | X    | X       | L     | X                 | S                              |
| Gold, silver             | S          | S       | X    | S       | S     | S                 | S                              |
| Nickel (dull)            | S          | S       | L    | S       | S     | S                 | S                              |
| Nickel (bright)          | S          | S       | L    | L       | S     | S                 | S                              |
| Tin, zinc                | S          | S       | X    | S       | S     | S                 | S                              |

temperatures. In general, the types of rubber that have best resistance to elevated temperatures also have the best resistance to oil and gas, although silicone rubber is an exception; Table 7.2 provides a rough guide to fitness for this use.

Two physical processes are involved in liquid uptake (absorption) by an elastomer. Liquids and gases dissolve in the surfaces of elastomers (adsorb) and penetrate further by diffusion. Since the rate of swelling is diffusion-controlled, the resistance to swelling of an elastomeric component increases as the square of its thickness and with increasing viscosity of liquid diffusants.

For gas or liquid as the penetrant, the initial surface concentration  $c_0$  is determined by the process of adsorption. With liquids,  $c_0$  is the equilibrium (maximum) mass uptake (also designated  $m_\infty$ ) ultimately attained throughout the elastomer – the solubility or equilibrium concentration – and is essentially independent of pressure. For gases, the adsorption process is dependent on pressure.

The rate of diffusion into the elastomer bulk is independent of pressure at normal pressures. However, a considerable effect of pressure shows up at high pressures, and this is illustrated to a marked degree in gas permeation. This phenomenon refers to the passage of gas right through an elastomeric sample; that is, it involves both surface solution (adsorption) and diffusion, and evaporation as the (anti)solution process on “the far side” of the sample.

Whether a particular elastomer absorbs large quantities of a low viscosity liquid depends on thermodynamic considerations. A drive exists for a liquid and a polymer to mix if a negative free energy change  $\Delta G$  takes place during the mixing. The free energy change is

$$\Delta G = \Delta H - T\Delta S \quad (7.8)$$

where  $\Delta H$  is the change in heat content (enthalpy),  $\Delta S$  is the change in entropy, and  $T$  is temperature. Thus, the requirement is that  $T\Delta S$  be greater than  $\Delta H$ . The enthalpy change is largely affected by solubility parameter  $\delta$  values for liquid and polymer [12], where  $\delta^2$  is the cohesive energy density, a measure of the energy of attraction between like molecules.  $\Delta H$  is less than  $T\Delta S$  only when certain conditions for  $\delta$  are met, for instance, if  $\delta$  values for an elastomer and a solvent are within about 1 to 2 (cal/cm<sup>3</sup>)<sup>1/2</sup> (2.05 to 4.1 MPa<sup>1/2</sup>) of each other. Then, considerable swelling can occur. If the liquid is a moderately viscous

oil, this maximum difference in  $\delta$  reduces to about  $0.8 \text{ (cal/cm}^3)^{1/2}$ . Practically, to avoid swelling, elastomer and liquid pairings with significantly different  $\delta$  values are used together. If this is not possible for other reasons, structural aspects, such as high crosslink density, high  $T_g$  (equivalent to low free volume), and high filler content among others, can reduce  $T\Delta S$  to oppose the effects of similar  $\delta$  values, and thus lessen swelling.

Figure 7.10 shows the degree of equilibrium swelling for a series of well-prepared samples of four common elastomers when immersed in solvents with a range of known  $\delta$  values. Diffusion is sufficiently fast at room temperature for equilibrium to be reached in a few days. This figure illustrates  $\delta$  values obtained for the elastomers of about 8 to 10  $(\text{cal/cm}^3)^{1/2}$ , obtained from solubility parameter spectroscopy (SPS), which employs solvent mixtures as the swelling media. The solvents are carefully chosen to avoid interactions, are completely miscible, and are mixed according to appropriate volume fractions to give many liquids of different, but known,  $\delta$  values. NBR has a high  $\delta$  value and is an oil-resistant elastomer. FKMs have even higher  $\delta$  values than NBR. The application of solubility parameters becomes more complex at values of about 15 to 23  $(\text{cal/cm}^3)^{1/2}$  because of hydrogen bonding effects, etc. This applies especially to water absorption. Many values of  $\delta$  (obtained in various ways) are listed in the literature for all common elastomers and liquids; a selection is shown in Table 7.4.

To repeat, the final concentration  $m_\infty$  is lower for a highly cross-linked or highly filled elastomer, even for a liquid of similar  $\delta$ . Another feature determining whether a liquid dissolves quickly in an elastomer is the liquid's viscosity; this can override solubility

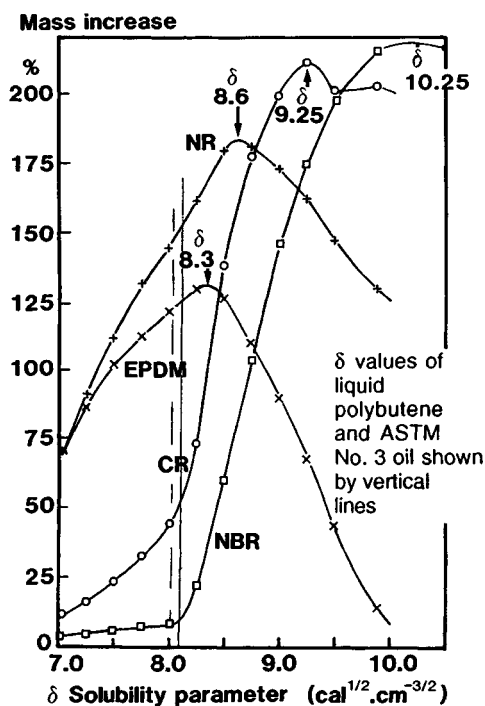


Figure 7.10 Solubility parameter spectra for four elastomers: NR, EPDM, CR, and NBR.

**Table 7.4** Solubility Parameter  $\delta$  Values for a Selection of Solvents at 20 °C

| Solvent             | $\delta$<br>(cal/cm <sup>3</sup> ) <sup>1/2</sup> |
|---------------------|---------------------------------------------------|
| Hexane              | 7.33                                              |
| Octane              | 7.60                                              |
| Decane              | 7.77                                              |
| Benzene             | 9.22                                              |
| Toluene             | 8.97                                              |
| <i>o</i> -Xylene    | 9.03                                              |
| <i>m</i> -Xylene    | 8.87                                              |
| <i>p</i> -Xylene    | 8.83                                              |
| 1,2-Dichloroethane  | 9.96                                              |
| Acetone             | 9.74                                              |
| Methyl ethyl ketone | 9.56                                              |
| Diethyl ether       | 7.74                                              |
| Ethyl acetate       | 9.10                                              |
| Methanol            | 14.52                                             |
| Ethanol             | 12.97                                             |
| Propanol            | 12.02                                             |
| Ethylene glycol     | 14.52                                             |

Source: G. Allen, G. Gee, and J. P. Nicholson, *Polymer*, **1**, 56 (1960)

parameter considerations. High molecular weight liquids cause both  $m_\infty$  and the rate of diffusion to be reduced considerably compared with typical solvents. The diffusion of liquids in elastomers is discussed in Section 7.6.2. The relationship of permeation, diffusion, and solubility for gases in elastomers is presented in Section 7.6.3.

### 7.6.1 Aqueous Liquids

All elastomers absorb some water over long periods of time. Only small amounts would be expected from  $\delta$  considerations which is usually the case. However, other factors can cause increases. Water absorption leads to an increase in mass and volume, but does not usually have much effect on the modulus or strength. However, stress relaxation can be significantly affected (see Section 7.2.3). Some compounding ingredients can leach out. For example, some antioxidants can be lost in this way, with a consequent loss of fatigue resistance under oxygenated conditions. Mass uptake measurements can be misleading if not corrected for mass loss effects by drying tests. Table 7.5 shows some typical (corrected) values for water absorption by some common elastomers after two years of immersion in seawater. Use of hydrophilic fillers or metal oxides in the cure system generally has a larger effect than polymer type. Thus, polychloroprene cured with litharge does not absorb much water, whereas polychloroprene cured with magnesium oxide absorbs large amounts. Conversely, if hydrophilic impurities are removed from a rubber, as in deproteinized natural rubber, the water uptake can be reduced (e.g., from 4% to 1% for NR).

Salt water is not generally a deleterious environment for rubber. If care is taken over certain points, a long and maintenance-free life can be expected for rubber engineering components, unlike the situation for metals, where corrosion needs to be constantly checked.

**Table 7.5** Water Uptake of Some Engineering Elastomers after Two Years in Seawater at 23 °C

| Elastomer                                  | Equilibrium<br>(% mass uptake of water) |
|--------------------------------------------|-----------------------------------------|
| Natural rubber                             | 4%                                      |
| Acrylonitrile-butadiene rubber             | 5%                                      |
| Polychloroprene cured with litharge        | > 5.5%                                  |
| Polychloroprene cured with magnesium oxide | > 32%                                   |

Polychloroprene has been used successfully for coating subsea pipes in offshore engineering applications to protect them from salt water corrosion. There are few reports of any problems, even after 10 years of service. This is currently the leading use of elastomers in offshore corrosion protection. Special polychloroprene compounds developed by the pipe coating manufacturers include ingredients to inhibit marine fouling.

In a case study made of a rubber tire after 42 years of exposure to seawater, the condition of the rubber was found to be still excellent. The tire was recovered from a shipwreck and sealed subsea to preserve all water uptake. Apart from some poor rubber-metal bonding to the carbon steel wires, there was no corrosion of the wires and no obvious deterioration of the rubber after 42 years in seawater [13]. Laboratory drying experiments showed that no more than 5% of water had been absorbed in this time. This value is in line with predictions from shorter term laboratory tests for this type of vulcanizate (natural rubber). This gives confidence in the ability of laboratory tests, accelerated by using thin-walled sections, to predict correctly the effects of seawater.

Natural rubber, sometimes blended with styrene-butadiene rubber, has been used to line water purification vessels used in power generation applications for more than 20 years, and although there may have been some long-term deterioration of the lining in purified water, nevertheless, protection of these vessels from large-scale corrosion has been very successful. Chlorobutyl rubber is frequently a better choice for such applications, since it combines relatively good adhesion when cured in situ at low temperatures with low water permeation.

Another case history that illustrates the excellent durability of elastomers in seawater is provided by the Hutton tension leg oil production platform (TLP) in the North Sea. This is a compliant structure with the compliance provided by a set of flex elements. Each flex element consists of bonded alternating layers of nitrile rubber and spherical section stainless steel reinforcements. A case study has been made [1] of the elements after five years of service. Figure 7.11 shows a schematic view of a similar component, a flex joint, illustrating its ability to sustain a conical angle displacement of 16°. The entire platform, with accommodation for 200 people, rests on the flex elements, which are structurally critical units. Such components should not be regarded as “off the shelf,” but the success of this project in a hostile region of the North Sea illustrates the reliability and durability of elastomeric components, provided there is adequate analysis and testing for the service environment. This included a fracture mechanics analysis, combined with extensive environmental and full-scale testing. So far, performance in service has been as predicted from the laboratory testing and fracture mechanics analysis. The nitrile rubber has shown excellent resistance to seawater with no measurable deterioration.

Ingress of water into the bulk of an elastomer is a diffusion-controlled process. This has been well studied, and at least the short-term aspects are understood [14]. Considering

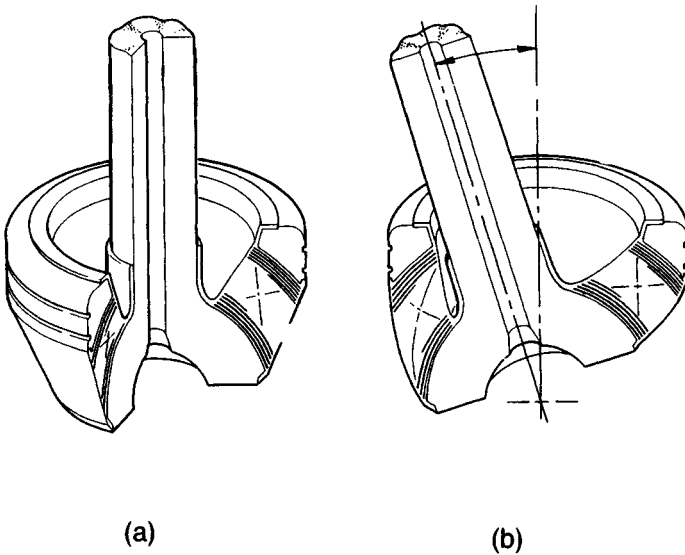


**Figure 7.11** Schematics for the Hutton TLP flex joint: (a) no deflection and (b)  $16^\circ$  conical deflection.

migration in natural rubber, water is only slightly soluble in the pure rubber hydrocarbon (since the two solubility parameters are very different). However, diffusing water collects around the hydrophilic impurities arising naturally in this elastomer, so that the overall water content reaches a level higher than would be expected. Droplets of water form and increase in size until their osmotic pressure is balanced by opposing elastic forces. After long times this effect progresses into the inner regions of the elastomer.

### 7.6.2 Hydrocarbon Liquids

As already noted, when a liquid contacts an elastomer, it adsorbs rapidly up to a concentration  $c_0$  at the surface, followed by diffusion of the liquid further into the elastomer. For adsorption, the thermodynamic drive is to equilibrate chemical potential of adsorbed and external liquid, the latter given by the liquid vapor pressure. For hydrocarbons and other nonaqueous liquids, diffusion dominates the movement of liquid into the elastomer bulk. In diffusive motion, individual molecules of the liquid move by “jumping” into adjacent free volume holes formed momentarily in the elastomer matrix during random thermal motions, arising from kinetic energy. The thermodynamic drive now is due to an attempt to equalize chemical potential (i.e., concentration) of the diffusing liquid throughout the elastomer.

The rate of this diffusive migration is governed by Fick’s laws of diffusion. These laws also apply if the diffusant is gaseous; the difference in mathematical treatment between gas-elastomer and liquid-elastomer systems lies in the different boundary conditions that are applied when Fick’s second law is integrated. If amount  $dm$  of substance diffuses across area  $A$  in time  $dt$  to give a concentration gradient  $dc/dx$ , Fick’s first law states

$$\left(\frac{1}{A}\right)\left(\frac{dm}{dt}\right) = -D\left(\frac{dc}{dx}\right) \quad (7.9)$$

where  $D$  is the diffusion coefficient (or constant) in square meters per second. By considering incremental increases in concentration along the path of the migrating species, Fick's second law is obtained:

$$\left(\frac{dc}{dt}\right) = D\left(\frac{d^2c}{dx^2}\right) \quad (7.10)$$

These equations assume  $D$  to be independent of concentration; however, for a small molecule diffusing in a polymer,  $D$  depends in reality on the local concentration and other conditions.  $D$  is affected inversely by the molecular size of diffusant.

As diffusion progresses, concentration-distance curves with shapes analogous to error function curves "erf  $z$ " develop. During this period, the average distance traveled by a particle in time  $t$  from  $x = 0$  is  $(2Dt)^{1/2}$ . The form of this expression indicates why, in practice, times of diffusion-related phenomena (e.g., swelling) increase with the square of elastomer thickness.

Mathematical solutions of Fick's second law are complex but have been obtained for many situations [15]. A current approach uses finite elements, with simple solutions applying to elements being summed for whole, complex, geometries. It is useful therefore to have one relatively easy means of determining  $D$  so that the result can be employed in finite element procedures for extrapolation to actual service conditions. This easy means of measurement is by mass uptake-immersion of sheet samples into the liquid of interest, and removal of these samples at appropriate time intervals for careful but rapid weighing before returning to the liquid.

To determine  $D$  for a sheet sample immersed in liquid, the solution of Fick's second law with appropriate boundary conditions gives

$$\frac{m_t}{m_\infty} = \left(\frac{2}{h}\right)\left(\frac{Dt}{\pi}\right)^{1/2} \quad (7.11)$$

where  $m$  represents mass uptake at time  $t$  and at equilibrium swelling, respectively, and  $2h$  is thickness. Eventually  $D$  becomes concentration-dependent as, after a while, liquid that has already entered the elastomer can contribute to the rate at which fresh liquid diffuses. One simple and convenient method of obtaining a representative value of diffusion coefficient is to measure  $D_{av}$ , an "average"  $D$ , at the point of 50% mass uptake, so that

$$0.5 = \left(\frac{2}{h}\right)\left(\frac{D_{av}t_{av}}{\pi}\right)^{1/2} \quad (7.12)$$

As for water uptake (Section 7.6.1), corrections for the leaching of soluble constituents out of the elastomer are made by reading values off desorption curves from drying tests performed on samples swollen to different degrees, and adding these values to the mass uptake curves at the appropriate times.

From the form of the equations above, plots of mass uptake versus square root of time should be informative. Figure 7.12 shows plots obtained when natural rubber sheet samples were immersed at 43 °C in liquid hydrocarbons of various viscosities. The portion

of the plots in the region around 50% mass uptake is apparently linear, permitting calculated  $D_{av}$  values to be obtained, representative of the diffusion rates. When samples near saturation, the rate of uptake diminishes until the equilibrium mass uptake value  $m_{\infty}$  is reached, signified by a plateau. Figure 7.12 illustrates the expected effect, namely that increases in viscosity clearly reduce diffusion rate and the magnitude of  $t_{av}$ . As a point of interest, the  $m_{\infty}$  “plateau” for the two lowest viscosity hydrocarbons show low but positive slopes. This observation is attributed to a secondary effect: the slow absorption of these hydrocarbon liquids by the proteinous, nonrubber content of natural rubber (the species that dominates water uptake in NR). This hypothesis is supported by repeating the experiment for one hydrocarbon liquid (ASTM No. 3 oil), but replacing NR by deproteinized natural rubber, to give a plot (shown in Fig. 7.12 by the dashed curve) displaying a near-equilibrium plateau for  $m_{\infty}$ . Table 7.6 shows the diffusion coefficients  $D_{av}$ , the equilibrium mass uptakes  $m_{\infty}$ , and associated equilibrium solubilities  $s_{\infty}$  for the four hydrocarbons in NR.

**Table 7.6** The Diffusion of Oil and Polybutenes into NR Elastomer at 43 °C: Sheet Samples, Nominal Thickness, 1 mm

| Diffusant      | Diffusion coefficient,<br>$D_{av}$<br>( $\text{m}^2/\text{s} \times 10^{-13}$ ) | Equilibrium mass uptake,<br>$m_{\infty}$<br>(%) <sup>a</sup> | Equilibrium solubility,<br>$s_{\infty}$<br>(g/mL) |
|----------------|---------------------------------------------------------------------------------|--------------------------------------------------------------|---------------------------------------------------|
| ASTM No. 3 oil | 12.5                                                                            | 136                                                          | 1.44                                              |
| Polybutene     |                                                                                 |                                                              |                                                   |
| $M_n$ 270      | 30.8                                                                            | 101                                                          | 1.07                                              |
| $M_n$ 780      | 2.1                                                                             | 48                                                           | 0.51                                              |
| $M_n$ 1300     | 1.9                                                                             | 28                                                           | 0.30                                              |

<sup>a</sup>Referred to initial sample weight

### 7.6.3 Hydrocarbon and Other Gases

While absorption measurements (involving weighings until the sample is saturated) are more convenient when assessing diffusion-related properties of elastomer/liquid systems, permeation measurements (involving passage of gas right through the elastomer) are more suitable when the fluid is gaseous. When an elastomeric polymer is exposed to gas at high pressure and the gas enters the bulk of the elastomer by the two-stage process of adsorption and diffusion, unlike the liquid case, the amount adsorbed is dependent on applied (partial) gas pressure. The diffusion stage is once again largely independent of pressure. In oil field engineering, pressures above 1000 atm can be met. Under these conditions, the amount of gas that enters the elastomer after a few days can be considerable, and if an elastomer is constrained, e.g., in a seal housing, and becomes saturated at equilibrium, this amount of absorbed gas again relates directly to applied pressure, as the concentration originally adsorbed is eventually achieved throughout the bulk.

The theory for absorption and permeation of fluids is well established [15–17] and concerns the interrelated processes of adsorption and diffusion. Adsorption of a single gas into the elastomer surface is governed by Henry’s law:

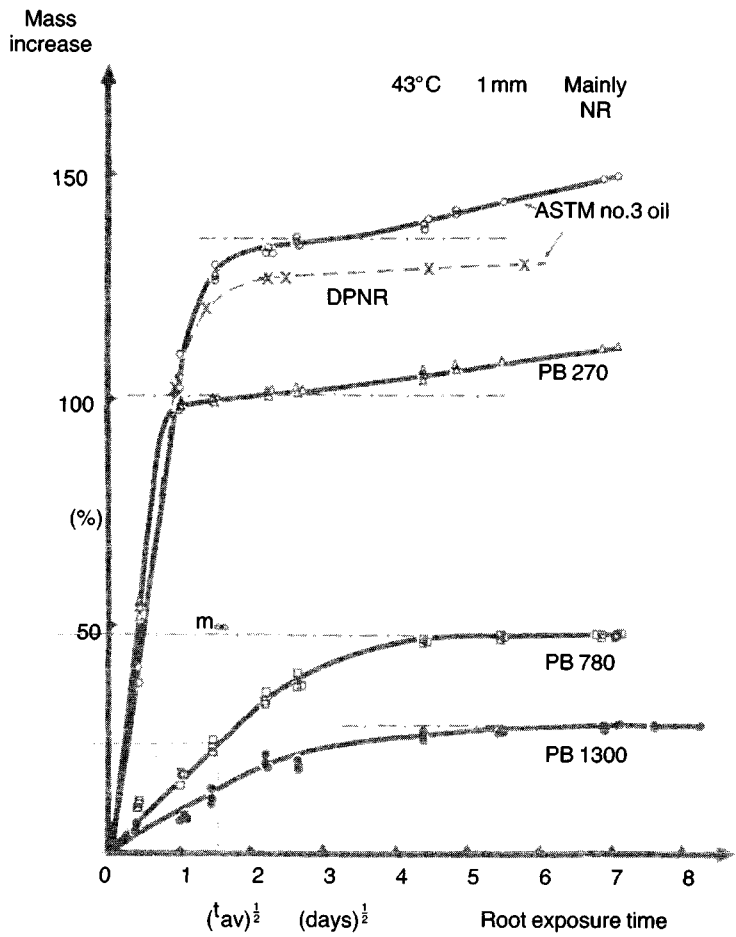


Figure 7.12 Typical hydrocarbon liquid diffusion in elastomers.

$$c = sP \tag{7.13}$$

where  $c$  is concentration,  $P$  is the applied gas pressure, and  $s$  is the solubility coefficient. To determine the concentration of one of the gases in the surface when a gas mixture contacts the elastomer, the partial pressure of that gas is employed in the expression above. This expression also applies to a liquid, but to its vapor pressure, not actual (hydrostatic) pressure: the former is only marginally affected by large changes in the latter, hence, the comment early in Section 7.6 that liquid solubility is essentially independent of pressure.

For gases, with vapor pressure normally equalling applied pressure, this expression suggests a linear relationship between concentration of dissolved gas and pressure *for all pressures*. Clearly this cannot be the case. The existence of limits can perhaps be most

easily visualized by considering that, at high pressures, gas densities reach comparable magnitudes to liquids. Hence, as for liquids, the vapor pressure no longer equals the actual gas pressure – it is much lower. As it is the vapor pressure that quantifies the driving force (chemical potential) for adsorption and hence permeation, eventually, at very high pressures, an equilibrium situation should be reached where further increases in pressure essentially cause no further increase in adsorbed concentration or permeation rate. From experience, Eq. (7.13) can be used at pressures of several hundred atmospheres, although some deviations in  $s$  are then possible.

Once molecules have been adsorbed (dissolved) in the elastomer surface, their diffusion into the bulk is generally independent of external gas pressure (except at high pressures, which cause compression of the elastomer and thus, in turn, change the rate of gas movement). As with liquids, the rate of diffusive migration is governed by Fick's law. For a plane sheet of elastomer, steady state diffusion of dissolved gas from one surface through to the other is given by an integrated version of Fick's first law:

$$\left(\frac{1}{A}\right)\left(\frac{q}{t}\right) = \frac{D(c_1 - c_2)}{h} \quad (7.14)$$

where a gas volume  $q$  diffuses through thickness  $h$  in time  $t$ ;  $c_1$  and  $c_2$  are the surface concentrations.

The process of permeation – the passage of gas from a high pressure region into, through, and out into the opposite low pressure side of an elastomer membrane – involves adsorption, diffusion, and evaporation. The last-named is treated in terms of negative adsorption on the low pressure side. By combining Eq. (7.13) and (7.14), we get for steady state permeation:

$$\frac{q}{t} = \frac{DsA(P_1 - P_2)}{h} \quad (7.15)$$

where condition 1 is the high pressure side and 2 is the low pressure side. The product of the coefficients  $D$  and  $s$  is termed the permeation coefficient (or permeability)  $Q$ :

$$Q = Ds \quad (7.16)$$

and

$$\frac{q}{t} = \frac{QA(P_1 - P_2)}{h} \quad (7.17)$$

This is the general gas permeation equation for a sheet at equilibrium (steady state) conditions. Hence, if an elastomer is employed in service as a diaphragm, hose lining, or O-ring, in a situation that permits gas to migrate through it, the equation immediately above (or a modified version allowing for different geometrical aspects) would apply.

Methods are known for measuring permeation rates at pressures up to 100 atmospheres or so [17], or even up to 1,000 atms [18]. When steady state permeation is attained, plots of  $q$  versus  $t$  give lines of gradient  $QA(P_1 - P_2)/h$ , so that  $Q$  can be calculated. At the onset, a certain time elapses before steady state permeation occurs. This transient stage has been used by Daynes to provide a separate determination of  $D$  [16]:

$$D = \frac{h^2}{6\tau} \quad (7.18)$$

where  $\tau$  is the time that the steady state line lags behind a line of the same gradient starting from the origin. After  $Q$  and  $D$  have been determined,  $s$  is easily obtained as  $Q/D$ . Knowledge of values of  $Q$  enables us to minimize the amount of gas that passes through a membrane or a thick-walled hose, for example. Knowing the value of  $D$  is helpful in estimating the average distance traveled in time  $t$  from  $x = 0$  using  $(2Dt)^{1/2}$ ;  $s$  affects explosive decompression, which is discussed later, because multiplying it by pressure gives the concentration  $c_1$  of gas present at the high pressure surface, from Henry's law, Eq. (7.13).

If the elastomer is used in an application with no outlet for the gas (e.g., as an inner lining inside a steel pipe), the equation governing gas adsorption applies, but subsequent migration of gas is governed by a solution of Fick's law using appropriate boundary conditions until the gas concentration reaches equilibrium throughout the elastomer; here the gas would be absorbed. Clearly, a permeation test for an unrestricted system can lead to a calculation of the amount of gas absorbed in a confined situation, as the  $c_1$  value for permeation equates with the eventual  $c_\infty$  value for absorption.

Elastomers for engineering use are obviously fully compounded, and some additives can affect permeation. The impact of ingredients that affect the degree of crosslinking is merely to alter the magnitude of coefficients such as  $Q$ , while retaining the form of equations given in earlier sections. Increasing the number of crosslinks decreases  $Q$ ; it is not known whether this results from changes in both  $D$  and  $s$  or just one of these coefficients.

The effect of carbon black and other fillers is more pronounced, causing a diluting effect, as well as increased "tortuosity" (i.e., the path length between and around filler particles). Both these effects decrease permeation rate. In addition, filler particles can adsorb diffusant molecules, to upset the normal behavior reflected in Fick's and Henry's laws.

Many data exist for the coefficients mentioned here. A selection is given in the Appendix, Table 5. As a result, permeation rates can be estimated for many service applications involving elastomers and gases at moderate pressures. However, it is often not valid to extrapolate these data to high pressures. High pressures can reduce the permeation coefficient dramatically [18], as shown in Fig. 7.13. A probable reason is that above certain pressures, the elastomer becomes compressed significantly and the free volume between polymer molecular chains decreases; hence, the diffusion rate decreases. This effect is displaced to higher pressures as the temperature is raised.

Added factors involved at high pressures are local strain effects and swelling effects. The latter are more often associated with liquid diffusion, but at high pressures, gas densities can approach liquid values.

Two phenomena frequently found in oil field applications that occur as a result of gas permeation are "explosive decompression" (ED) and "doming." When an elastomer is saturated as a result of exposure to high pressure gas, or approaches this condition, rapid removal of the high pressure means that the situation quickly becomes one of supersaturation. The amount of gas present now exceeds the concentration applying to the new low external pressure. The excess gas possesses a thermodynamic drive to come out of solution, and it can do so by collecting at existing or incipient flaws, or initiating

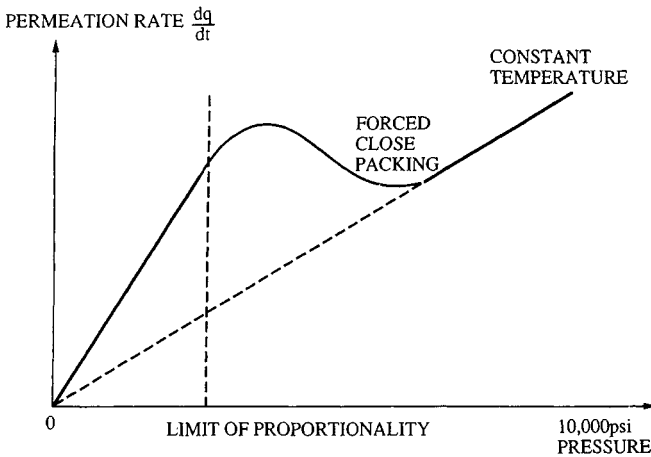


Figure 7.13 High pressure gas permeation in elastomers.

nucleation processes that lead to flaws. The continued arrival at the flaws of more gas by diffusion leads to bubble growth. At some threshold value, this growth causes fracture, and subsequent expansion of the flaw includes tearing as a major component. This is the phenomenon of explosive decompression. It causes an elastomer to become unable to seal, for example. Carbon dioxide, which is highly soluble in many elastomers, is particularly likely to cause this effect.

When gas is driven out of solution near a bonded interface in a composite structure, the bonding can be fractured in an analogous way; this is the phenomenon of doming, which can force the linings of flexible pipes to collapse into the flow passage. These phenomena are the subject of research [19–21]. Some techniques to minimize the ED problem include reducing the amount of gas present by choosing low-solubility high-diffusion elastomers or introducing mechanical constraints; and increasing the resistance to bubble growth and fracture by increasing the modulus and tear strength of the elastomer. However, as indicated in Section 2.3.1.3, increasing one of these properties normally causes the other to deteriorate. Biphasic, single component, elastomers have recently been developed to bring about both optimizations [22]: with these, an interwoven IPN-type structure of two phases of the same elastomer at different states of cure is proposed to satisfy the above requirement. Explosive decompression resistance has increased significantly in these elastomers compared to existing seal materials.

#### 7.6.4 Effects of Temperature and Chemical Attack

Two basic forms of chemical aging exist: continuation of cure at elevated temperatures due to unstable cure systems, and exposure to hostile fluids (the latter occurring initially at the elastomer surface, depending on diffusion to access the bulk unless surface cracking provides a more rapid route). The ubiquitous role of oxygen and ozone has already been discussed. In the oilfield industry, hostile fluids can include hydrogen sulfide (produced in

some wells) and various amines and amides used as corrosion inhibitors. The former can attack unsaturated sealing elastomers such as nitriles, so that use of hydrogenated nitrile rubbers (and FKM)s can be beneficial here. Even some of the FKM)s are prone to attack by amines at high temperatures, a process accelerated by application of stress (presumably the increase in stored energy also increases chemical potential). This is an instance of environmental stress cracking (ESC), which can involve chemical or physico-chemical attacks; the correct FKM should be selected for the application. Similarly, some FKM)s are attacked by methanol by a process which can be shown to be reversible – and the application of stress again exacerbates it.

When a diffusant can also chemically react with the elastomer matrix, two questions arise.

- Are some diffusant molecules deactivated by the chemical interaction, so that the overall diffusion rate decreases?
- Is the chemical reaction aggressive enough to embrittle and/or break up the elastomer?

Such questions can be resolved only by experiments. Both the physicochemical and hostile chemical processes can be governed by Arrhenius-type equations. Hence, for diffusion coefficient  $D$ , we write

$$D = D_o \exp\left(\frac{-E_d}{RT}\right) \quad (7.19)$$

where  $D_o$  is a frequency factor correlating with the initial concentration dependence of  $D$ ,  $T$  is temperature,  $R$  the gas constant, and  $E_d$  is the activation energy for diffusion. Similar equations apply for  $s$  and  $Q$ . Tests show that the expected linearity from this equation in plots of  $\log Q$ , etc., versus  $1/T$  does frequently occur in practice.

In addition, an Arrhenius equation applies to the kinetics of chemical reactions:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (7.20)$$

where  $k$  is the rate of chemical reaction, the frequency factor  $A$  is now concerned with molecular collisions, and the activation energy  $E_a$  is the critical energy needed for reactions to occur. Regarding the attack of hostile fluids on high molecular weight elastomers, it can be tentatively assumed from statistical network theory that applied stress (and associated modulus or stiffness magnitudes) vary directly with elastomer crosslink density to a first approximation. Hence, the kinetics of reaction (classically based on concentrations of reactants and/or products) can be followed by changes in stiffness or modulus. In accelerated aging tests, one means of representing  $k$  is by measuring time ( $1/k$ ) to a point at which a chosen property has changed by a specified amount, say, 20%. The commonly cited law that chemical reaction rates more-or-less double with every 10 °C increase in temperature is attributed to an appropriate  $E_a$  value applying to these reactions; the reader is invited to determine this  $E_a$  value in one of the problems listed at the end of the chapter where the true picture is seen to be more complicated.

One complication is that interaction of diffusion and chemical reaction, with their different activation energies, could mean that the 50% property change occurs because the deterioration is shared quite evenly throughout the elastomer (i.e., rapid diffusion, slow chemistry) or that it occurs because the outer regions only have degraded extensively (i.e., slow diffusion, rapid chemistry). Empirical solutions are necessary in this area.

### 7.6.5 Effect of Radiation

Most elastomers increase in hardness when irradiated, but butyl and polysulfides soften and become liquid. Free radical mechanisms are involved; an analogous phenomenon prevents peroxide curing of these two elastomers. Carbon black filled vulcanizates are more resistant to radiation than unfilled vulcanizates. Table 7.7 indicates the radiation resistance of some elastomers.

The incorporation of protective agents, known as antirads, can improve resistance by an order of magnitude. When rubbers are irradiated and then compressed at high temperatures, they generally acquire high compression set.

**Table 7.7** Radiation Stability of Elastomers

|                                    | Damage:<br>Utility of rubber: | Incipient to<br>mild<br>Nearly always<br>usable | Mild to<br>moderate<br>Often<br>satisfactory | Moderate<br>to severe<br>Limited use |
|------------------------------------|-------------------------------|-------------------------------------------------|----------------------------------------------|--------------------------------------|
| Rubber                             | Gamma exposure dose (kJ/kg)   |                                                 |                                              |                                      |
| Polyurethane rubber (AU, EU)       |                               | 70                                              | 280                                          | 1670                                 |
| Natural rubber (NR)                |                               | 15                                              | 310                                          | 1670                                 |
| Adduct rubbers <sup>a</sup>        |                               | 24                                              | 200                                          | 820                                  |
| Styrene-butadiene rubber (SBR)     |                               | 15                                              | 108                                          | 420                                  |
| Fluororubber (Viton) (FKM)         |                               | 30                                              | 200                                          | 650                                  |
| Cyanosilicone rubber <sup>a</sup>  |                               | 30                                              | 100                                          | 320                                  |
| Vinyl pyridine rubber <sup>a</sup> |                               | 25                                              | 80                                           | 250                                  |
| Nitrile rubber (NBR)               |                               | 15                                              | 50                                           | 170                                  |
| Chloroprene rubber (CR)            |                               | 15                                              | 34                                           | 100                                  |
| Chlorosulfonyl polyethylene (CSM)  |                               | 8                                               | 25                                           | 80                                   |
| Fluororubber (Kel-F) (FKM)         |                               | 20                                              | 44                                           | 83                                   |
| Silicone rubber (Q)                |                               | 11                                              | 27                                           | 63                                   |
| Polyacrylate (ACM)                 |                               | 10                                              | 22                                           | 54                                   |
| Butyl rubber (IIR)                 |                               | 16                                              | 25                                           | 42                                   |
| Polysulfide rubber (TR)            |                               | 3                                               | 12                                           | 26                                   |

<sup>a</sup>Specialty materials

## 7.7 Durability of Rubber-Metal Bonds

Many elastomeric-based components involve composite structures with the elastomer (rubber) strongly bonded to steel or another metal. Using suitable adhesives, rubber-

metal bonds are usually formed during vulcanization of the rubber and are generally as strong or stronger in dry conditions than the rubber itself; thus, when failure does occur (e.g., on a pull-to-failure test), it occurs through the rubber (often denoted as 100% R) for a good bond. In that case, a precise quantitative measure of bond strength is not possible, but it is probably not necessary for practical purposes. With most rubbers, the occurrence of *dry* rubber-metal bond failure usually indicates a manufacturing process error, but in some cases (e.g., some FKM elastomers) the bond strength may be moderate only. Prolonged exposure to liquids (especially aqueous liquids) can however, cause failure of an initially strong bond. Only “hot formed bonds” produced during the vulcanization of the rubber are durable in water; cold bonded systems (e.g., with epoxy resins or cyanoacrylates, even when applied to oxidised surfaces to enhance wetting) usually give weaker initial bonds and more rapid deterioration in service environments.

### 7.7.1 Adhesion Tests

There are a number of tests for rubber-metal bond strength, but the simplest and most effective are probably the double-shear test and the peel test, as depicted in Fig. 7.14. Since fracture mechanics solutions exist for both test piece geometries, interfacial bond strength can be measured in fundamental terms, and the fatigue life of the adhesive bond can be analyzed for cohesive failure of the rubber itself. The double-shear test piece has advantages when it is desired to maintain a constant shear strain on the adhesive joint during an environmental exposure test, for example, to simulate specific mechanical aspects of service conditions. For general characterization of bond strength and durability, however, the peel test is usually more convenient. It can also be adapted for testing of samples applied “on site” (e.g., of pipe linings or coatings) as a quality control (QC) check.

For the peel test piece, peel energy  $P$  is expressed as follows:

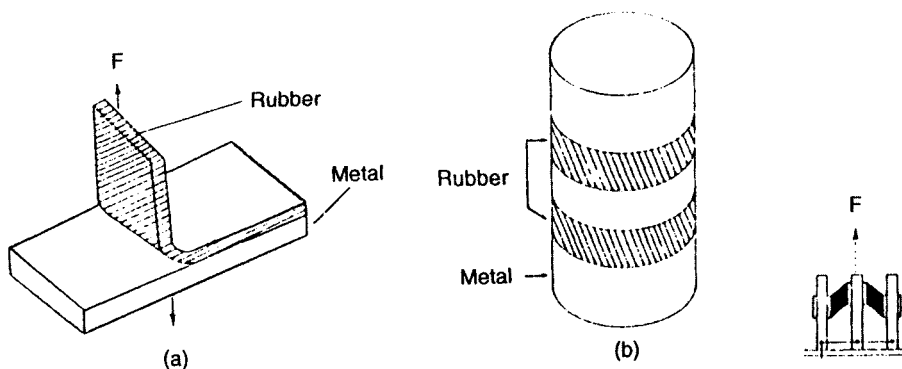


**Figure 7.14** Test piece geometries for rubber-metal bond tests: (a) peel test at 90° and (b) double-shear test.

$$P = \frac{F}{w}(\lambda - \cos \Phi) - Uh \quad (7.21)$$

where  $U$  is strain energy density in the peeled leg,  $\Phi$  the peel angle,  $\lambda$  the extension ratio,  $h$  the unstrained strip thickness,  $w$  the width of the peel strip, and  $F$  the peel force.

For linear stress-strain behavior, Eq. (7.21) can be rewritten [23]:

$$P = \frac{F}{w}(1 - \cos \Phi + e/2l) \quad (7.22)$$

where  $e$  is the elongation (displacement) at force  $F$ , and  $l$  the original elastomer tab length. Thus, all factors are obtainable from original dimensions or readings from the test force versus elongation trace. At  $90^\circ$ , Eq. (7.22) reduces to:

$$P = \frac{F}{w}(1 + e/2l) \quad (7.23)$$

In the case of linear stress-strain behavior, and if the peel leg is constrained to be approximately inextensible so that  $\lambda = 1$  or  $e = 0$  (e.g., by incorporating fabric backing or cutting the test piece sufficiently wide) then generally:

$$P = \frac{F}{w}(1 - \cos \Phi) \quad (7.24)$$

and, for  $\Phi = 90^\circ$ ,  $P = F/w$ , and at  $\Phi = 180^\circ$ ,  $P = 2F/w$ .

Tests performed at  $180^\circ$  avoid inaccuracies due to changes in the peel angle during the test. For thick peel strips, however, lower peel angles avoid inaccuracies due to bending of the peel strip during testing. At low angles, forces can be high, and breaking the tab is common. A useful compromise angle is  $90^\circ$ .

A recently developed double peel test, which rotates through a wide range of angles during testing, has been shown to give, during the early stages of rotation, dry rubber-metal bond failure even for well-bonded systems – those giving rubber failure with normal peel tests [24]. This is a useful feature for mechanistic studies but, clearly, is a geometry to be avoided when designing bonded rubber/metal composite components.

### 7.7.2 Rubber-Metal Adhesive Systems

There are a number of proprietary rubber-metal primers and adhesives available. The most widely used and researched system is the Chemlok 205 primer and Chemlok 220 adhesive (or equivalent) supplied by Lord Corporation (USA), Durham Chemical (UK), and Henkel (Germany). For some synthetic elastomers (e.g., fluoroelastomers), specialty adhesives are now available. For fluorocarbon elastomers, Chemlok 607 is recommended, and for hydrogenated nitrile elastomers, Chemlok 233, using Chemlok 205 metal primer in each case. Nitrile rubber bonds well to this primer alone. Fluorosilicone elastomers are more difficult to bond, and new adhesives are under development.

The methods of applying primers and adhesives are important, and it is recommended that appropriate adhesive tests be performed during component development. For critical

engineering components, peel tests should be performed on a QC basis during production. An acceptable level of adhesion strength from QC tests then “signs off” a production batch.

Three factors of key importance in ensuring bond durability are:

- Good initial procedure for degreasing, grit blasting, and metal surface preparation
- Strict quality control for application of primer and bonding agent
- Use of an appropriate cure schedule for the rubber component (time, temperature, and pressure during cure) with regard to the adhesive system selected

Good initial bonds, formed in the circumstances above, can remain intact even after several years of immersion in salt water. Some factors affecting durability, such as electrochemical potentials, are discussed in the next section.

### **7.7.3 Durability in Salt Water: Role of Electrochemical Potentials**

It is almost certainly beneficial to cover all metal parts of a structural bearing with several millimeters of rubber. This substantially retards both metal corrosion processes and bond failure mechanisms. If sacrificial anodes are used to protect adjacent steelwork, the bond edge should be encapsulated in rubber and electrically isolated where possible.

Although well-made rubber-metal bonds can be extremely durable, it has been shown [25] that if the metal adherends are not inert, then rapid bond failure can occur. The highest potential (commonly used in engineering applications of cathodic protection) is provided by a zinc sacrificial anode in combination with carbon steel adherends. This produces a measured cathodic potential of 1040 to 1070 mV at the rubber-metal interface (with reference to a silver-silver chloride reference electrode). Bond failure is then rapid at all temperatures tested, but there is no corrosion of the carbon steel.

A failure surface consists in general of three regions. There is a first region where failure occurred through cohesive fracture of the rubber. Adjacent to this region of polymer fracture is a gray region where failure is predominantly at the interface between the metal and its primer coating. The third region is of bond failure, occurring in situ during exposure, before the pull-to-failure test was performed.

When determining any change in adhesive bond strength (interfacial failure energy), it is important to know whether there is any change in the cohesive strength of the polymer. Clearly if the rubber tear strength decreased during water exposure, the area of bond failure could be anomalously lower than if it had remained constant. To investigate this, the energy required to cause fracture may be measured by integrating the force-deflection curve from a shear pull-to-failure test. This energy can then be used to derive a characteristic stored energy density  $U$  at fracture. In the absence of bond failure,  $U$  characterizes the critical fracture energy of the polymer, and indeed, yields a value comparable to results from standard fracture or tear tests. With an area of partial bond failure, however, the fracture geometry is more complicated, although the same approach can be used.

The characteristic stages of the bond failure process are illustrated in Fig. 7.15, where bond failure penetration depth is plotted against the square root of seawater exposure time. If diffusion processes are involved, a linear relation between penetration depth and the square root of time is expected from diffusion theory.

The first stage is a time lag observed before any bond failure is measured (i.e., 0.5 mm failure penetration depth). This "induction period" increases with decreasing potential and decreasing temperature. The second stage is a period of increasing area of bond failure as an approximately linear function of the square root of exposure time (days). This suggests that liquid diffusion is a controlling factor, although only diffusion along the interface is considered important, not (unlike the case for organic coatings) diffusion through the bulk polymer. A failure penetration rate can be defined for each test condition. Finally, there is an approach to an "equilibrium" depth of bond failure.

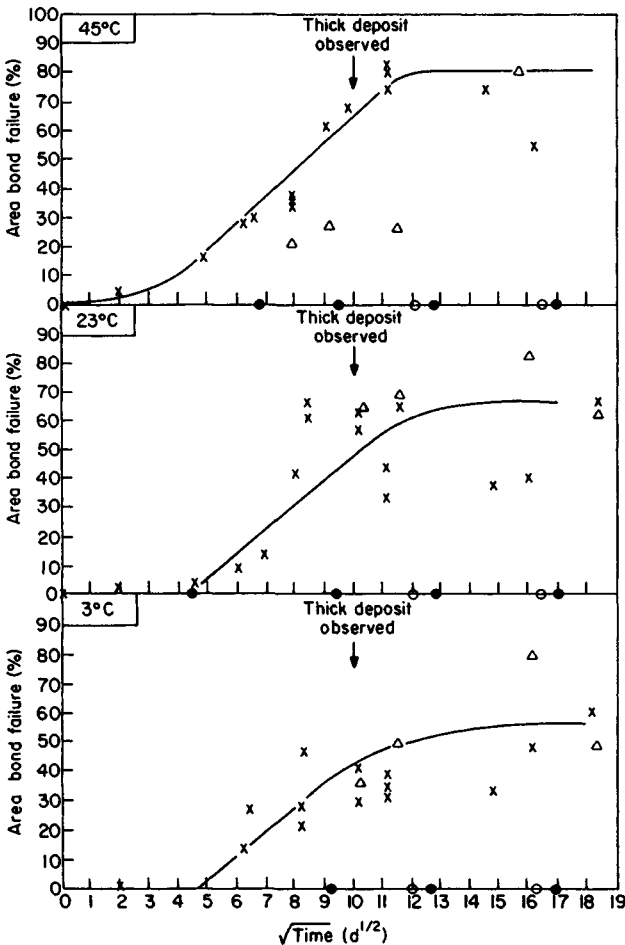


**Figure 7.15** Bond failure rates in seawater with cathodic potentials of 1.05 V; Test pieces are NR-carbon steel with C205/C220 adhesive system.

The effect on carbon steel test pieces of potential differences lower than 1.05 V may be characterized by a potentiostatic arrangement to supply a constant impressed current at a chosen potential difference (e.g., 0.95, 0.85, 0.75, and 0.61 V) at the bond edge.

Induction period increases as the level of imposed cathodic potential is reduced, for example, from one day at 1050 mV to 30 days at 610 mV for NR-steel test pieces [25]. After the induction period, bond failure begins, and the failure penetration rates are approximately the same for all potentials. After very long exposure periods (up to three years), the penetration depth for NR-steel with C205/C220 approached an equilibrium value, which increased from 4 mm at 610 mV to the maximum possible ( $\geq 12.5$  mm) at 1050 mV. Identical test pieces exposed to sea water in the same restraining jigs but without electrical connection to a potentiostat or to a dissimilar metal (i.e., 0 mV) showed no bond failure whatsoever, even after more than three years of seawater exposure.

The effect of dissimilar metals in contact can be similar, as a result of local potential differences set up by differences in the galvanic series. Adherends of Inconel, two types of titanium, and stainless steel were exposed to seawater at 3, 23, and 45 °C in holding jigs of carbon steel. The system was not electrochemically inert for the Inconel, stainless steel, or titanium test pieces, and the possibility existed of electrochemical interactions throughout the seawater exposure period. Different metals contacting steel showed different rates of bond failure [25].

It has recently been found that the rate of bond failure is not necessarily accelerated by higher exposure temperatures. In some cases, higher rates of bond failure have been found at lower temperatures. This is due to a variety of interacting environmental factors [26].

## 7.8 Life Prediction Methodology

Quantitative prediction of the durability of an engineering component becomes an increasingly important requirement as elastomers are used for more critical engineering applications. Life prediction methodology embraces all aspects of processes that may affect the function of the component. The first step is to define the function of the component clearly enough for a failure criterion to be derived. This criterion may be an unacceptable change in stiffness for a bearing or antivibration device, unacceptable leakage for a sealing component, or unacceptable crack depth. Definition of the failure criterion requires an understanding of the engineering end use. Examples follow for possible failure criteria for oilfield production applications [27]:

- Increase or decrease in stiffness to values outside design limits (e.g. for hoses, seals, flex elements)
- Occurrence of surface cracks
- Dynamic growth of service cracks to unacceptable limits (e.g., for flex elements, flex joints)

- Formation of cracks/blisters in bulk (e.g., from explosive decompression, for seals, flex joints)
- Loss of sealing stress by stress relaxation (seals, end-fittings for hoses)
- Extrusion of seal/hose lining into surrounding gap
- Weakening by excessive swelling (and effects on factors above)
- Excessive build-up of gas due to seal leakage (from factors above or thermal changes) and permeation
- General degradation (hoses, seals, in extremely hostile fluids).

After the failure criterion has been defined, the changes in the elastomer material that could cause this failure may be analyzed. Durability of rubber components can be defined quantitatively on this basis. Crack growth is clearly one such change, age hardening is another, and swelling in or permeation of fluids is another. Fracture mechanics analysis of the rubber layer(s) in the component is the only known way of predicting crack growth rates in elastomeric components. This approach has a documented track record of successful application to actual components [1, 3, 4, 5].

Further work is needed to extend the range of geometrical solutions to which fracture mechanics can be applied, and there is some discussion of this in chapters 5 and 6. Other changes in the material (e.g., oxidative age hardening) may affect rates of crack growth. Alternatively, there may be no crack growth but only hardening in the material. Liquid ingress could cause weakening; gas ingress could cause explosive decompression fracturing. Whatever the mechanism, each process needs to be identified and its rate characterized separately. Only then can interactions between different mechanisms be considered for life predictions on a sound basis.

Tests on materials should be performed at different levels of severity and at different time intervals, to ensure that the rate of change is measured. Changes in physical properties over many years are described in [28]. Care must be taken to match the test conditions to the service conditions in as realistic a way as possible. For example, if measurements of rate cannot be made at the service temperature in the time available, accelerated tests may be used at elevated temperatures or increased frequency, provided a clear proof exists that the acceleration is an actual increase in rate of the same process. This point needs to be validated for each material. After the rate of each process has been determined under the accelerated condition(s), the rate at the service condition may be determined by extrapolation. It is conventional to use an Arrhenius plot of log (failure rate) against reciprocal temperature to enable extrapolations to be made to long times (low rates) at lower temperatures.

After each process is separately understood in this way, interactions can be put together to provide a life prediction of the durability of the component under service conditions. This should then be validated by selected prototype testing. Figure 7.16 is a flow diagram for the complete life prediction methodology used at Materials Engineering Research

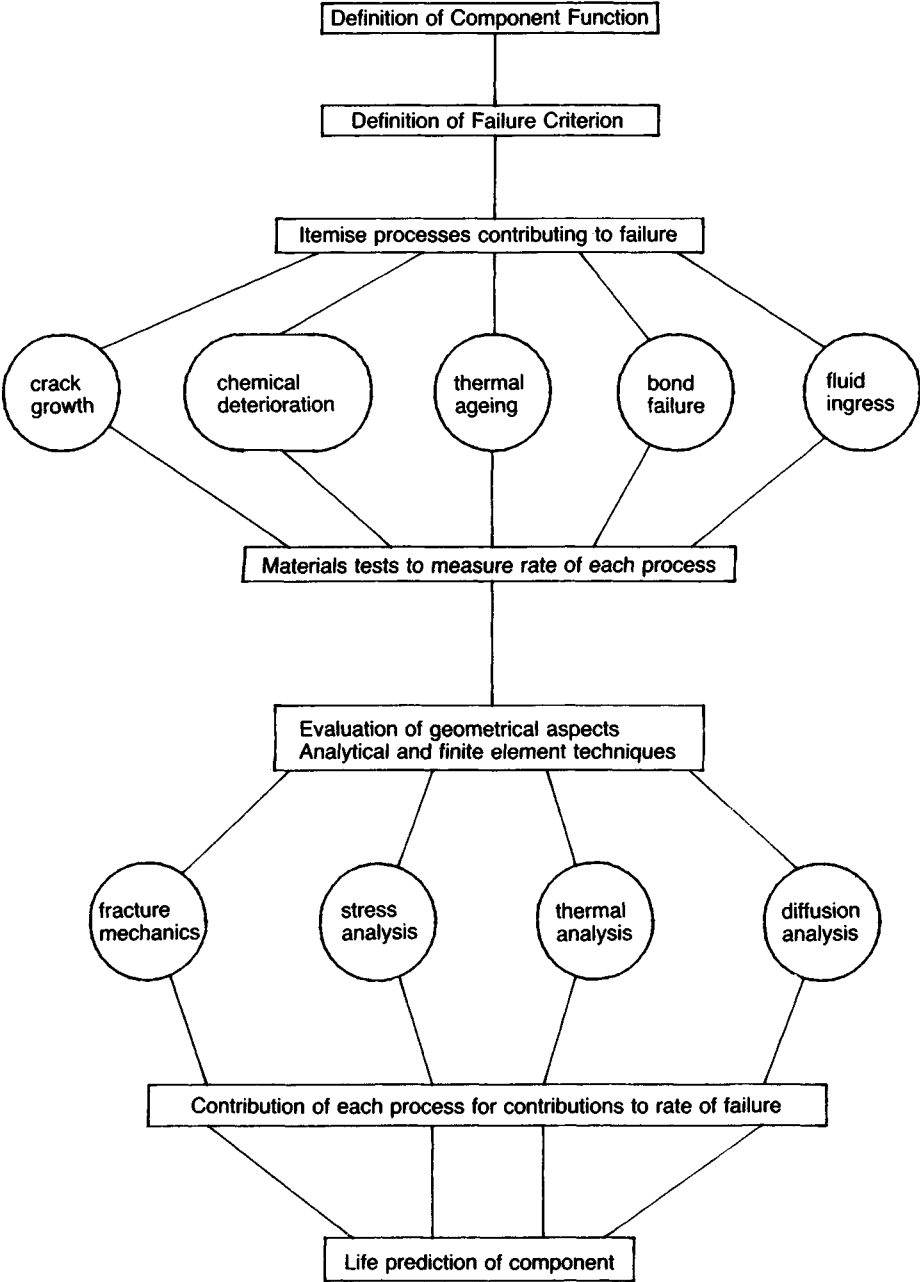


**Figure 7.16** Flow diagram for life prediction methodology to establish rubber engineering component durability.

Laboratory to estimate the durability of a polymer engineering component. This approach has provided a useful basis for development work on several types of components. Once all relevant parts of the life prediction chart have been characterized, the database also provides a sound basis for computer-aided design, which can eventually model durability processes to reduce the need for complex and costly prototype testing.

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## References

1. A. Stevenson and W. McIntosh, "Operating Experience with Elastomer Composites on the Hutton Tension Leg Platform," in *Proceedings of the Ninth International Conference on Offshore Mechanics and Arctic Engineering*, Houston, February 1990. Published by American Society of Mechanical Engineers, New York (1990).
2. A. Stevenson, "Rubber in Engineering," in *Kempes Engineering Yearbook (1986-90)*, Morgan Grampian Publishers, London, Chapter C3.
3. H. L. Oh, *Rubber Chem. Technol.*, **53**, 1226 (1980).
4. R. F. Breidenbach and G. J. Lake, *Phil. Trans. R. Soc. London, Ser. A*, **299**, 189-202 (1981).
5. D. G. Young, presentation at American Chemical Society, Rubber Division Conference (1989).
6. A. Stevenson, "Longevity of Natural Rubber in Structural Bearings," *Plast. Rubber Process. & Appl.*, **5**, 253 (1985).
7. A. N. Gent, *J. Appl. Polym. Sci.*, **6** (22), 442 (1962).
8. C. J. Derham, *Rubb. India*, **16** (Oct. 1974).
9. C. J. Derham, *J. Mater. Sci.*, **8**, 1023 (1973).
10. C. J. Derham and R. A. Waller, *The Consulting Engineer*, **39**, 49 (1975).
11. D. Cumberland, Panama Weathering Study, Dupont Technical Report 515 (1983).
12. J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, *Regular and Related Solutions*, Van Nostrand Reinhold, New York (1970).
13. K. Ab-Malek and A. Stevenson, *J. Mater. Sci.*, **19**, 585 (1984).
14. E. Southern, in A. Stevenson, Ed., *Rubber in Offshore Engineering*, Adam Holger, Bristol, UK, Chapter 19 (1984).
15. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, Oxford (1956).
16. G. J. van Amerongen, "Diffusion in Elastomers," *Rubber Chem. Technol. (Rubber Rev.)*, **37**, 1065 (1964).
17. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London (1968).
18. R. P. Campion, Proceedings of Corrosion 91, NACE, Cincinnati, paper 456 (1991); also (with G. J. Morgan) *Plastics, Rubber & Composites Processing & Applications*, **17** (1), 51-58 (1992).

19. R. P. Campion, *Cellular Polymers*, **9** (3), 206 (1990).
20. A. Stevenson and G. J. Morgan, *Rubb. Chem. And Technol.*, **68** (2), 197 (1995).
21. B. J. Briscoe, T. Savvas and C. T. Kelly, *Rubb. Chem. And Technol. (Rubb. Reviews)*, **67** (3), 384 (1994).
22. R. P. Campion and B. Thomson, *Offshore Research Focus*, 114 (publ. OSO, Glasgow, UK), p. 5 (Oct. 1996).
23. R. P. Campion and P. J. Corish, "Elastomer – Metal Adhesion Processes" in P. J. Corish, Ed., *Concise Encyclopedia of Polymer Processing & Applications*, Pergamon Press, Oxford, UK, 211–216 (1992).
24. R. P. Campion, *American Chemical Society, Rubber Division*, Fall Meeting, Cleveland, Ohio, paper 24 (Oct. 1997).
25. A. Stevenson, *J. Adhes.*, **21**, 313–327 (1987).
26. A. Stevenson and B. Thomson, *Proceedings of Rubber/Metal Bonding Conference*, Frankfurt, Germany (Dec. 1998), publ. RAPRA, Shawbury, UK (1998).
27. R. P. Campion, *Proceedings of Elastomer – Service Life Prediction Symposium '98*, publ. ARDL, Akron, Ohio, paper C (Sept. 1998).
28. R. P. Brown and T. Butler, "Natural Ageing of Rubber", Rapra Technology Ltd., Shawbury, UK, 2000.

## Problems for Chapter 7

1. A building mount consists of three rubber layers bonded between horizontal steel plates. Each rubber layer is 15 mm thick, and rectangular in cross-section: 200 mm x 600 mm. The shear modulus  $G$  of the rubber is 0.99 MPa. When the mount is loaded to 2070 kN (taking 1 minute), the initial compressive deflection is 6.9 mm. Calculate the compression stiffness of the mount. (Obtain a check to this answer to within about 5 MN/m using the bearing dimensions and rubber properties provided in Chapter 8, Section 8.2. Use interpolated shear modulus and associated values from Table 8.1, and allow for the contribution from bulk compression.) If the physical creep rate  $A$  is 6.6% per decade and the chemical creep rate  $B$  is 0.47% per year at the average service temperature of 20 °C, what is the expected creep after 1 year, 5 years, 10 years, 20 years, and 50 years? When does the amount of chemical creep equal the amount of physical creep? How long does it take for the total deflection to reach 12 mm?
2. Briefly discuss factors to be considered in selecting rubbery materials for sealing against:
  - (a) hydrocarbon liquids such as ASTM No. 3 oil at (i) 80 °C (ii) 180 °C (iii) –30 °C.
  - (b) sea water at 80 °C
  - (c) methanol at 80 °CFrom information given in this chapter, if NR sheets are immersed in ASTM No. 3 oil for one year at 43 °C, how far does the oil penetrate into the rubber on a root-mean-square basis?
3. (a) Two reactions each possess the same activation energy  $E_a$  but their rates differ at the same temperature. Explain this in terms of the Arrhenius equation.

- (b) If a chemical reaction has a value for  $E_a$  of 21 kcal/mol, how much faster does the reaction proceed at 160 °C compared with 140 °C, taking the gas constant  $R$  to be 1.987 cal/deg/mol?
- (c) As a rough rule of thumb, it is often stated that increasing the temperature of a reaction by 10 °C doubles its rate. By constructing Arrhenius-type plots for the temperature range 20 to 180 °C, compare the “doubling” method with a true Arrhenius approach and see if you can calculate an equivalent  $E_a$  value (in kcal/mol and kJ/mol) for this range. Also determine equivalent  $E_a$  values for the smaller temperature ranges: (i) 20 °C to 40 °C, and (ii) 160 °C to 180 °C. Comment on your findings.
4. Thin strips of a rubber sample were exposed at an elevated temperature to a chemically-hostile liquid which saturated the strips in a few days, causing some swelling. Strips were removed at intervals of time and low-strain tensile moduli were obtained immediately at 23 °C. The whole procedure was repeated for exposures at two other temperatures. The values obtained for tensile moduli are given below.
- It can be seen that the modulus changes in three stages: first decreasing, then increasing, and finally decreasing again. Explain how this might be. Determine activation energies for three cases: (a) the early minimum modulus, (b) the maximum modulus, and (c) the original modulus level when it is achieved again following the maximum. N.B. One of these cases will require a time-based extrapolation.
- According to an Arrhenius prediction, how long would it take to attain these three levels of modulus at 60 °C in the same fluid. Comment on your degree of confidence in the findings.

Modulus Values (MPa)

| Temp<br>(°C) | Time (days) |     |     |     |      |      |    |    |     |      |      |      |
|--------------|-------------|-----|-----|-----|------|------|----|----|-----|------|------|------|
|              | 0           | 1   | 3   | 5   | 7    | 14   | 28 | 56 | 84  | 112  | 140  | 168  |
| 160          | 10          | 8.5 | 8   | 10  | 12.5 | 12.5 | 10 | 9  | 8.5 | 8    | 7.5  | 7.5  |
| 140          | 10          | 9   | 8.5 | 8   | 8.5  | 10   | 14 | 12 | 10  | 9    | 8.5  | 8    |
| 120          | 10          | 9.5 | 9   | 8.5 | 8    | 8    | 9  | 12 | 15  | 14.5 | 13.5 | 12.5 |

5. A series of gas permeation tests gave the following results for CO<sub>2</sub> passing through a rubber sheet (Eq. 7.16 to 7.18):

Determine the activation energies of permeation, diffusion and solubility for this system. In an application, the rubber is to be exposed to CO<sub>2</sub> gas at 345 atm and 70 °C until saturated and then the external pressure will be rapidly removed. Assuming that there is a critical gas concentration  $c_c$  of 200 cm<sup>3</sup> (S.T.P) per cm<sup>3</sup> of rubber at 70 °C, above which explosive decompression (ED) failure is probable, determine whether this critical value will be exceeded. What other factors influence failure by explosive decompression?

| Temperature<br>(°C) | Q<br>(m <sup>2</sup> /s/atm)<br>× 10 <sup>-10</sup> | D<br>(m <sup>2</sup> /s)<br>× 10 <sup>-10</sup> | s<br>(atm <sup>-1</sup> ) |
|---------------------|-----------------------------------------------------|-------------------------------------------------|---------------------------|
| 195                 | 4.1                                                 | 23.0                                            | 0.18                      |
| 155                 | 2.6                                                 | 10.0                                            | 0.26                      |
| 130                 | 1.8                                                 | 5.2                                             | 0.35                      |
| 100                 | 1.1                                                 | 2.0                                             | 0.55                      |

## Answers to Problems for Chapter 7

1. Compression stiffness = 300 MN/m.

Taking  $t_0$  as 10 min, the amount of creep (increase in deflection) is 2.2 mm, 2.6 mm, 2.9 mm, 3.4 mm, 4.55 mm, respectively, after the given periods under load.

Time for creep contributions to be equal = 94 years.

Time for total deflection to reach 12 mm = 117.5 years.

2. (a) On a solubility parameter basis, NBR, HNBR, FKM or perfluoroelastomer FFKM can be chosen; NBR is the cheapest but HNBR has the best mechanical properties. (FFKM is expensive but becomes necessary at temperatures above 200 °C. TFE/P copolymer can also be used above 200 °C because, even though the value of  $\delta$  is only 9 (cal/cm<sup>3</sup>)<sup>1/2</sup>, this polymer is resistant to swelling by oil for structural reasons.) Hence,

(i) NBR (or HNBR if high strength is required)

(ii) FKM or FFKM

(iii) Low-acrylonitrile NBR, so that  $T_g$  is below -30 °C

(b) Most elastomers not containing hydrophilic groups are suitable (ECO or high acrylonitrile NBR are examples that would not be recommended). Also, some curing systems (e.g., litharge-cured CR) and hydrophilic fillers should be avoided.

(c) NBR, HNBR. Some FKMs; others swell excessively; contact the manufacturer for advice.

Penetration distance = 8.9 mm, by applying the expression  $(2Dt)^{1/2}$  and using the appropriate value for  $D$  from Table 7.6.

3. (a) The two reactions have a different frequency factor  $A_0$ .  $E_a$  does not predict actual rates – only how the rate of a particular reaction changes from one temperature to another.

(b) A factor of 3.26 faster. (Apply Eq. 7.20 to the two temperatures, and subtract.)

(c) Taking the rate  $k$  at 20 °C to be unity and doubling 16 times to 180 °C gives values for plotting as the natural logarithm  $\ln k$  against reciprocal temperature  $1/T$ . The result is clearly not linear but it might be considered near enough for a reasonably linear fit to be obtained (statistical  $r^2 = 0.986$ ). From the slope ( $-E_a/R$ ) of the best-fit straight line, a value of  $E_a$  is obtained of 18.3 kcal/mol (= 76.6 kJ/mol). However, from the slopes at the temperature extremes, we have

(i)  $E_a = 12.6$  kcal/mol (= 52.9 kJ/mol) for the temperature range 20 °C to 40 °C

(ii)  $E_a = 27.3$  kcal/mol (= 114.1 kJ/mol) for the temperature range 160 °C to 180 °C

Obviously, the “doubling” rule of thumb only applies over a very limited temperature range.

4. An initial softening occurs due to swelling. A secondary crosslinking reaction, brought about by the chemically hostile species, then dominates the second stage. A degradation reaction, causing softening again, takes over during the third stage, perhaps due to absorbed oxygen or involving a product of the second-stage crosslinking.
  - (a) 10.5 kcal/mol. (b) 17.5 kcal/mol. (c) 18.0 kcal/mol, after extrapolating the property versus time plot to give a time of 238 days to a third-stage modulus of 10 MPa.
  - (a) 118 days. (b) 13 years. (c) 42 years. Ideally, many more repetitions of this aging test, preferably involving more temperatures and times, are required to give adequate confidence in the longer predictions because a small error in  $E_a$  can make a large difference in a predicted value over a long time. It can be the case (e.g., in oil field engineering) that major construction goes ahead irrespective of the status of prediction tests for rubber components, so that only a few data points are available for prediction purposes. It is imperative under these circumstances to use error bars to indicate the worst-case prediction.
5. From best-fit lines,  $E_a(Q) = 4.82$  kcal/mol;  $E_a(D) = 8.92$  kcal/mol; and  $E_a(s) = -4.07$  kcal/mol. Reasonable agreement with Eq. (7.16) is thus demonstrated. From an Arrhenius extrapolation  $s = 0.865 \text{ atm}^{-1}$  at  $70^\circ\text{C}$ , so that at 345 atm,  $c = 298 \text{ cm}^3/\text{cm}^3$ . Hence, the limit  $c_c$  is exceeded and ED would be expected to occur. (Note that the existence of such a limit is not yet established.)

See last paragraph in Section 7.6.3 for other factors affecting ED.